

that since the annealing temperatures are all above the onset of deuterium desorption from the fully covered Ru surface,³ the anneal results in a significant drop in the surface coverage of deuterium. This is shown in the inset in Fig. 1 which is a plot of the integrated areas under the desorption spectra in Figs. 1(b)–1(e), relative to the area of a saturation coverage of deuterium. The important observation, however, is that annealing prior to Cu evaporation results in the appearance of a new desorption peak at ≈ 400 K, similar in temperature to deuterium desorption from the clean Ru(0001) surface.

As mentioned earlier, the additional desorption feature at ≈ 400 K when deuterium is annealed prior to Cu evaporation can be attributed to deuterium occupying subsurface sites on the Ru(0001) surface. We have previously shown that the population of these sites is preferential for H atoms compared to D atoms during a 10 K s^{-1} temperature ramp on a Ru(0001) surface precovered with a coadsorbed H/D layer, resulting in retarded H_2 (and HD) desorption.¹ However, slower thermal annealing populates the subsurface sites with both isotopes and eliminates this kinetic isotope effect. In fact, the 400 K (β_2) D_2 desorption peak shifts by ~ 20 K to higher temperature upon annealing compared to a similar D_2 coverage on an unannealed surface³ accounting for the absence of the isotope effect. When 1–2 ML of Cu are evaporated onto a Ru(0001) surface precovered with adsorbed hydrogen (deuterium), the H_2 (D_2) desorption occurs well below 300 K as demonstrated in Fig. 1(a) and in Ref. 4. However, the movement of deuterium atoms from the subsurface sites to the surface is apparently unaffected by the Cu overlayer, still occurring at temperatures near 400 K. Upon exiting the subsurface region, deuterium spills over onto the Cu film, recombines, and desorbs. Recombination and desorption must occur rapidly since the crystal temperature is well above that required to desorb deuterium from the Cu overlayer as indicated by the desorption trace in Fig. 1(a). Thus, this series of processes accounts for the new desorption feature at ≈ 400 K in Figs. 1(b)–1(e). The separation between the desorption due to surface and subsurface deuterium upon Cu deposition in the TPD spectra then allows their relative populations to be quantified.

The amount of deuterium desorbing at 400 K increases with annealing temperature initially, subsequently falling at temperatures above 322 K for a 90-s anneal.³ The maximum population for deuterium in this subsurface state is $\approx \frac{1}{4}$ ML.

This behavior can be understood in terms of the two competing processes occurring simultaneously during the thermal anneal: (1) movement in and out of the subsurface sites (from and to the surface), and (2) desorption from the surface. As pointed out in our previous paper,¹ the onset of penetration into the subsurface site and desorption both occur at ≈ 300 K for saturation hydrogen coverages on Ru(0001). However, the latter process (desorption) results in a continual loss of deuterium from the Ru surface (Fig. 1, bottom) depleting both the surface and subsurface populations.

Integration of the peak areas in Figs. 1(b)–1(e)³ indicates that the ratio of the subsurface deuterium population (400 K desorption) to the deuterium remaining on the surface after the anneal [$\theta_D(400\text{ K})/\theta_D(300\text{ K})$] as a function of temperature rises initially to a constant value (determined to be $\approx 0.9 \pm 0.2$). Further, we found that once this population ratio is obtained, it is roughly independent of the time of the anneal as well as the temperature.³ This behavior indicates that an equilibrium is established between the surface and subsurface populations after a 90-s anneal at temperatures above ≈ 320 K. That the equilibrium populations of surface and subsurface D atoms are nearly equal and that the population ratio (≈ 1) is independent of temperature implies that the binding energies for deuterium in surface and subsurface sites for total coverages below $\frac{1}{2}$ ML are approximately equal.

Acknowledgments: The authors wish to thank the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for the support of this work. One of us (J. T. Y.) thanks Sandia National Laboratories for a summer visiting faculty appointment. This work, performed at Sandia National Laboratories, was supported by the U. S. Department of Energy under Contract No. DE-AC04-76DP00789.

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Summary Abstract: K-resolved inverse photoemission study of Pd/Nb(110)

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(Received 12 October 1987; accepted 30 November 1987)

The study of metallic interfaces or thin films is currently an area of considerable interest. It has been demonstrated that such films may show unusual catalytic or adsorption behavior¹ or, in the case of ferromagnetic materials, unusual mag-

netic properties.² One interface that has received considerable attention is the niobium palladium interface.³ It has been shown that palladium deposited on the niobium(110) surface grows epitaxially up to 1 monolayer (ML) and then

undergoes a first-order phase transition into a face-centered-cubic (fcc) (111) structure.⁴ Photoemission studies of this interface indicate that for the monolayer coverage there is a reduction in the density of states at the Fermi level, producing an electronic structure that is essentially noble metal like. Indeed it has been demonstrated that this surface is totally inert to the adsorption of carbon monoxide unless cooled to < 100 K.⁵ Inverse photoemission studies indicate the presence of a new unoccupied state in the interface.⁶ This state which is located ~ 1.6 eV above the Fermi level is two dimensional in character having no dispersion with k_{\perp} . In this paper we extend these studies by reporting our inverse photoemission observations of the palladium monolayer produced by annealing thick palladium films.

Our studies were carried out on an inverse photoemission apparatus that has been described in detail elsewhere.⁷ Briefly it consists of a grating spectrograph capable of detecting photons in the range 10–30 eV and a custom-built electron source giving a momentum resolution of the order of 0.1 Å. A single-crystal Nb(110) surface was produced by repeatedly annealing a niobium foil to 2000 °C. Palladium was then evaporated from a tungsten boat and the deposition monitored by both Auger electron spectroscopy and a quartz-crystal monitor.

As in the earlier studies the thick palladium films are found to grow with the fcc (111) direction normal to the surface.⁴ Indeed as shown in Fig. 1 the surface clearly shows both the Shockley and image states previously identified in the L_2, L_1 band gap.⁸ Annealing the surface to higher and higher temperatures removes the palladium overlayers with the slow emergence of states associated with the niobium substrate. It will be seen in Fig. 1 that after annealing to 800 °C there is no longer any evidence of the structure, identified earlier as an image state suggesting that the feature, identified before as a surface state will also have disappeared. Annealing to 1000 °C leaves the equivalent of 1 ML of palladium on the surface as determined by Auger electron spectroscopy. It will be seen that the surface shows the same state at 1.6 eV above the Fermi level as was previously seen following the deposition of 1 ML of palladium by evaporation. We therefore suggest again that this state is characteristic of the bond between the niobium and palladium.

Examination of the spectrum from 1 ML produced by annealing the thick palladium film shows that the niobium d state centered at 3.5 eV above the Fermi level is of lower intensity when compared with the equivalent band following the evaporation of a palladium monolayer. Spectra recorded at different incident electron energies show the same general trend of a reduction in intensity from this substrate Σ_4 band. We suggest that this difference indicates that slight alloying occurs for the annealed surfaces. Indeed similar conclusions have been reached in core level studies of annealed palladium films on a tantalum substrate.⁹

In summary we have identified what we believe is an unoccupied antibonding state in the interface between niobium and palladium. This state is found for both the evaporated palladium monolayer and annealed palladium films. However, our studies indicate that in the case of the annealed films the palladium tends to alloy with the niobium.

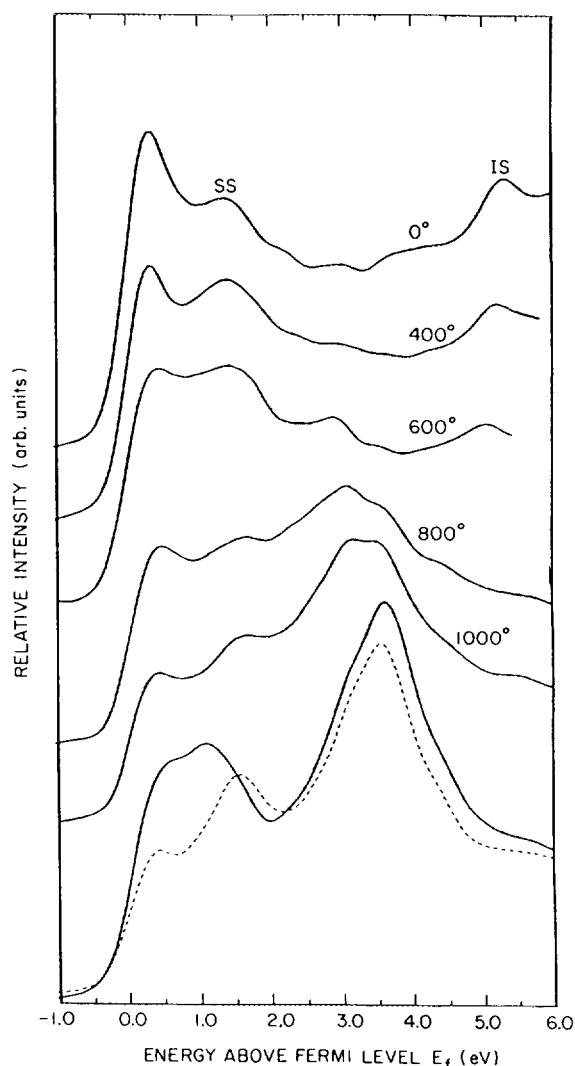


FIG. 1. Inverse photoemission spectra recorded from different palladium films produced by annealing a thick palladium film to the temperature indicated. The lowest two curves are (—) clean niobium and (---) evaporated palladium monolayer. In all cases the incident electron beam energy is 16.85 eV with respect to the Fermi level.

Acknowledgment: This work was supported by the Division of Materials Sciences, U. S. Department of Energy, under Contract No. DE-ACO2-76CH00016.

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